Electrorheology of Suspensions of Variously Protonated Polyaniline Particles under Steady and Oscillatory Shear

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Abstract:

Electrorheological (ER) and dielectric properties of silicone-oil suspensions of polyaniline (PANI) particles protonated with phosphoric and tetrafluoroboric acids to various doping level have been investigated. The particle conductivity was thus varied between the order of 10^{-9} S/cm and 10^{-4} S/cm. The dynamic yield stresses obtained at controlled shear rate mode viscometry, the storage moduli from the oscillatory shear experiments and the dielectric relaxation times from frequency dependences of dielectric constant and loss factor were used as criteria of rigidity or elasticity of ER structures and particle mobility in the electric field. The conductivity of suspension particles plays a decisive role in their ER behaviour. The ER efficiency increased as conductivity of dispersed particles raised, irrespective of the type of employed acid used for the protonation of PANI.

Zusammenfassung:

Elektrorheologische (ER) und dielektrische Eigenschaften von Suspensionen aus Silikonöl und Poly(anilin)-Partikeln, die mit Phosphor-und Tetrafluorborsäure in unterschiedlicher Stärke protoniert wurden, wurden untersucht. Die Leitfähigkeit der Partikel wurde in der Größenordnung von 10^{-9} S/cm und 10^{-4} S/cm variiert. Die dynamische Fließpannung, die durch Messungen in dem Modus der kontrollierten Scherrate erhalten wurde, der Speichermodul aus oszillatorischen Scherversuchen und die dielektrischen Relaxationszeiten aus der Frequenzabhängigkeit der dielektrischen Konstanten und des Verlustfaktors wurden als Kriterium der Starrheit oder der Elastizität der ER-Strukturen und der Partikelbeweglichkeit in dem elektrischen Feld verwendet. Die Leitfähigkeit der Suspensionspartikel spielt eine entscheidende Rolle in ihrem ER-Verhalten. Die ER-Wirksamkeit nahm mit der Leitfähigkeit der dispergierten Partikel zu, unabhängig von der zur Protonierung von PANI verwendeten Säure.

Résumé:

Nous avons étudié les propriétés electrorhéologiques (ER) et diélectriques de suspensions de particules de polyaniline (PANI) protonées avec des acides phosphoriques et tétrafluoroboriques à divers degrés de dopage. La conductivité de la particule a donc ainsi été variée entre 10^{-9} S/cm et 10^{-4} S/cm. Les contraintes dynamiques de seuil obtenues en mode de vitesse de cisaillement contrôlée, les modules élastiques obtenus à partir des expériences de cisaillement oscillatoire et les temps de relaxation diélectrique obtenus à partir de la dépendance fréquentielle de la constante diélectrique et du facteur de perte, ont été utilisés comme critères de rigidité ou d'élasticité des structures ER et de mobilité de la particule dans le champ électrique. La conductivité des particules en suspension joue un rôle décisif dans leur comportement ER. L'efficacité ER augmente avec la conductivité accrue des particules dispersées, sans relation avec le type d'acide utilisé pour la protonation des particules PANI.

Key words: polyaniline, electrorheology, steady shear, oscillatory mode, protonation

1 INTRODUCTION

Electrorheological (ER) effect [1], known as an outstanding change in rheological behaviour of ER suspension after the application of external electric field has been attracting strong attention since its discovery 60 years ago. The particles randomly dispersed in the non-conducting carrier medium are polarized in the presence of the electric field, resulting in particle fibrillation with string-like or columnar structures oriented along the field direction. In the electric field of intensity of several kilovolts per millimetre, this abrupt change sets in order of milliseconds. Thus, a dramatic increase in viscosity of several orders of

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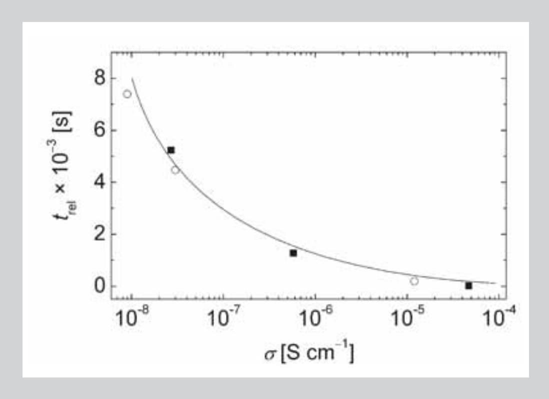

Figure 10: The dependence of relaxation time, t_{rel} on the conductivity, σ of the PANI particles. PA (solid) and TA (open symbols).

of the higher conducting particles, the conductivity is an important factor controlling their mobility in the electric field. Measured dielectric values were approached by virtue of Havriliak-Negami empirical Equation [36].

$$\epsilon^* = \epsilon'_\infty + \frac{\left(\epsilon'_o - \epsilon'\right)}{\left(1+\left(i\omega t_{rel}\right)^a\right)^b} \tag{2}$$

Here, ϵ'_o and ϵ'_∞ are the limit values of relative permittivity at the frequencies below and above the relaxation frequencies, t_{rel} is a relaxation time, a is the scattering degree of t_{rel} and b is related to the asymmetry of the t_{rel} spectrum. Large values of a mean a great scattering of t_{rel}. When a differs much from zero and b significantly from unity, the t_{rel} spectrum becomes more asymmetrical. In our case, however, the spectra are practically symmetric and the parameter b tends to one. Thus the Havriliak-Negami Equation changes to the Cole-Cole Equation

$$\epsilon^* = \epsilon'_\infty + \frac{\left(\epsilon'_o - \epsilon'_\infty\right)}{1+\left(i\omega t_{rel}\right)^a} \tag{3}$$

often successfully used for evaluation of dielectric properties of ER suspensions [37, 38].

4 CONCLUSIONS

Our findings revealed, that protonation of PANI particles with various acids at a same relatively high protonation degree may provide material with different ER property. On the other hand, conductivity of particles proved to be a universal factor controlling both viscoelastic properties of the suspension material as well as particle mobility in the electric field.

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